

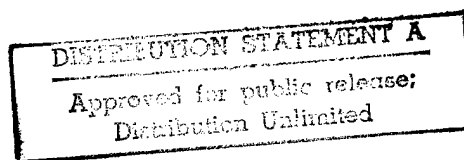
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# Japan Report

SCIENCE AND TECHNOLOGY



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# JAPAN REPORT SCIENCE AND TECHNOLOGY

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## BIOTECHNOLOGY

### LATEST STUDIES ON SYNTHETIC ENZYMES REVIEWED

Tokyo BIO INDUSTRY in Japanese Jul 86 pp 22-30

[Article by Kenjiro Hattori, assistant professor, Department of Engineering, Tokyo Institute of Polytechnics: "Synthetic Enzymes--Molecular Level"]

[Text] The history and current trends in research into synthetic enzymes will be reviewed in this paper, making reference to reports published over the last few years (chiefly comprehensive reports written in Japanese).

#### 1. Lessons From Natural Enzymes

All chemical reactions within cells are catalyzed by enzymes, which elevate the reaction rates to levels necessary for the maintenance of life. In this sense, enzymatic reactions can be regarded as a treasure house of very minute chemical reaction systems. From a functional point of view, natural enzymatic reactions have the following three major characteristics:

- (1) High efficiency: They exert high catalytic activity under mild conditions in the living body;
- (2) Specificity (distinction among molecules): They select only specific molecules from a given mixture of compounds and catalyze only specific reactions;
- (3) Regulation: They are capable of regulating various stages of reactions, such as their initiation and completion, and of effecting changes in reactive pathways.

Enzymes are made of high-molecular-weight proteins. To date, X-ray diffraction analysis of the three-dimensional crystalline enzyme structure has disclosed the following features:

- (1) Presence of catalytic sites: Catalytic sites are the functional groups which exert chemical catalytic actions on substrate molecules; an understanding of which is helped by concepts of organic reaction mechanisms. Frequently, nonprotein coenzyme molecules and metallic ions are associated with catalytic sites.

(2) Presence of binding sites: At binding sites, reversible incorporation of substrates takes place, via various intermolecular interactions. Hydrophobic cavities have been found in the microenvironment of binding sites. In addition to the interactions between hydrophobic groups, ionic and hydrogen bonds are also known to be important in substrate incorporation.

From accumulated data concerning natural enzymes, we can propose a scheme for the essential enzymatic reaction mechanisms. For example, cytochrome P-450 (a natural oxidizing enzyme) is thought to involve the factors and structure shown in Figure 1.

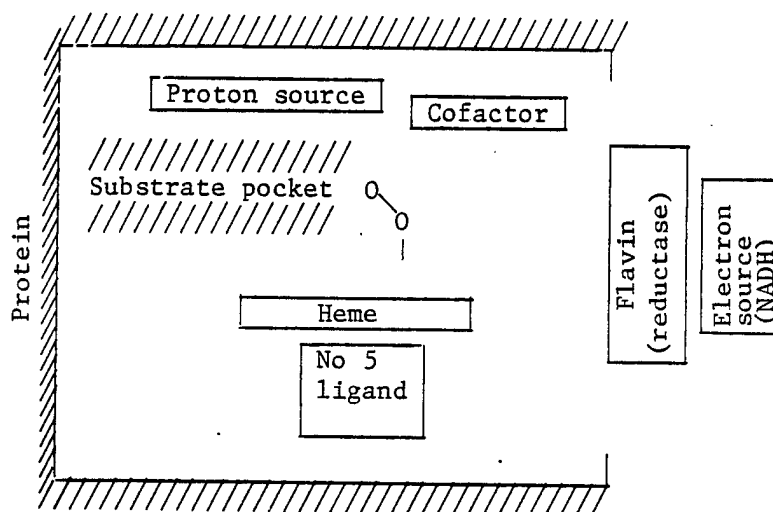


Figure 1. Factors Related to Cytochrome P-450

## 2. Trends in Model Synthetic Enzyme Studies

Learning the structures and functions of natural enzymes, as they are elucidated by investigators, we cannot help wondering at the minute detail of nature. So far, studies of synthetic enzymes have proceeded in two directions, each utilizing the techniques of organic synthetic chemistry. The goals of these two differ slightly, but their findings are complementary.

In one direction, research is aimed at testing the validity of essential hypotheses regarding the structure and function of natural enzymes. This type of study, a field of whose investigators interpret each enzymatic reaction as a complicated combination of organic concepts and terms. If some model synthetic enzymes, designed on the basis of a presumed mechanism for natural enzymes, can even partially exert the natural functions, it means success in our understanding of these features. In many cases, synthetic enzymes are capable of exerting only partially the functions of natural enzymes. As long as only the partial functions are compared, it is not rare for synthetic enzymes to be comparable or superior to natural enzymes.

In a second direction, research is aimed at obtaining synthetic enzymes for practical use. Also in this type of research, synthetic enzymes only partially exert the functions of their natural counterparts. However, it is possible for them to satisfy the requirements for industrial use. So that if a synthetic enzyme is to be used industrially as a lower-cost substitute for a natural enzyme, it needs to satisfy the following requirements: 1) A synthetic enzyme must exert a specific catalytic action sufficiently similar to its natural equivalent; and 2) the substrates, on which a synthetic enzyme acts, must be qualitatively or quantitatively important compounds. Additional requirements are synthesizing ability, durability and wide applicability. In the future, it will become possible to design total molecular systems, using a combination of synthetic enzymes. It is not impossible using synthetic enzymes to construct a bioreactor chemical plant. Nowadays, more than 100 basic studies on synthetic enzymes are made public every year. Many of these studies seem to be potentially applicable to industry.

### 3. Various Approaches to Synthetic Enzymes

Several approaches which have been highlighted mainly over the last few years will be described below. They have been selected chiefly from comprehensive reports written in Japanese. Readers, who want to know more detail are advised to refer to the original papers.

#### 3.1 Synthetic Enzymes Obtained by Gene Recombination

An amino acid at a particular position in an enzyme can be transformed (site-directed mutagenesis). For example, Perry of Genentic Co. transformed the Ile-3 of T<sub>4</sub> lysozyme into Cys and as a result strengthened the S-S bridge. In this way, the thermal stability of the enzyme was improved so that it did not become inactive even when exposed to 67°C for 2 hours (Figure 2).



Figure 2. T<sub>4</sub> Lysozyme in Which Transformation of Ile-3 Into Cys Resulted in an S-S Bridge Formation \*active site

Bulow incorporated beta-galactosidase and galactokinase genes into *Escherichia coli*, resulting in the expression of a chimeric enzyme. In this

way, they obtained an enzyme capable of efficiently transforming lactose directly into galactose phosphate in the presence of ATP.

### 3.2 Semisynthetic Enzymes Obtained by Chemical Mutation

By chemically modifying a particular site on a natural enzyme, semisynthetic enzymes with a new function have been obtained. Kaiser of the Rockefeller University transformed papain (a hydrolase) into an oxidoreductase by modifying the Cys residue of papain's active site with a flavin derivative. In this study, the catalytic site was transformed without changing the hydrophobic pocket of the original enzyme (Figure 3). A weak point in this technique is that it can be applied only to particular reactions under restricted conditions of organic synthesis.

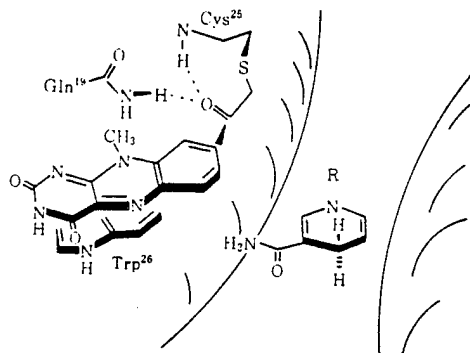


Figure 3. Active Site of a Semisynthetic Enzyme

A dihydronicotinamide molecule of the substrate has been incorporated into the hydrophobic pocket.

### 3.3 Synthetic Enzymes (Synzymes) Developed Using High-Molecular-Weight Carriers

The term "synzyme" was first used by Klotz in his report on studies into hydrolase polyethylene imine which has imidazole in its side chain. Research on synzymes has been increasing in recent years.

Mosbach of Lund University and Maeda of the Fermentation Research Institute tried to develop synthetic enzymes, using high molecules as carriers of nicotinamide adenine dinucleotide (NAD) or its phosphate ester (NADP), which are coenzymes for many oxidoreductases. Recently, Okada of Osaka University obtained excellent coenzyme activity by linking these compounds to the terminus of polyethylene glycol (Figure 4). Further, Pandit immobilized 1,4-dihydronicotinamide group with a polystyrene resin and used it for the reduction of acridine, obtaining a reproductive efficiency of 93 percent.

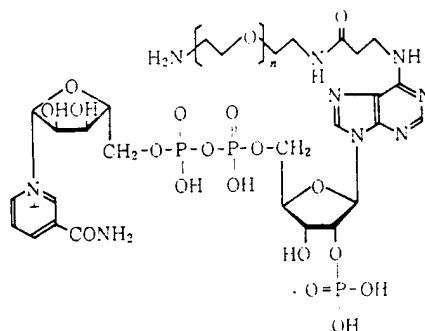


Figure 4. Polyethylene Glycol-Linked NADP

### 3.4 Synthetic Enzymes Using Clathrate Compounds

The development of synthetic enzymes using clathrate compounds is now the most active research area. Research has been gathered from the viewpoint of host-guest complexes having a definite microstructure. Also from a functional point of view, many synthetic enzymes, produced using clathrate compounds, have been attracting attention. Japan leads the world in this field of research both in quality and quantity. Recently, an international conference on clathrate chemistry was held, and the proceedings have been published.

#### (1) Synthetic Enzymes Using Cyclodextrin (CD)

There have been many trials into the production of synthetic enzymes using cyclodextrin, which consists of natural cyclic oligosaccharides. Recently, the author and co-workers have found that methylated CD works as an effective catalyst for ATP production. This compound can be regarded as a mimic of adenylate kinase; it may be applied as a subreactor for ATP-requiring reactions (Figure 5).

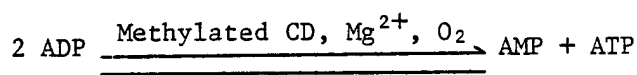


Figure 5. Adenylate Kinase Mimic Using Methylated CD

According to Breslow, thiazolium-linked CD accelerates tritium replacement or oxidation of aromatic aldehydes. A chymotrypsin mimic, developed by Bender, has a more precise enzyme model; the reaction speed achieved by the use of this model was almost equal to that of natural enzymes (Figure 6, Table 1). More recently, a study by Breslow of pyridoxamine-bound CD, which is used not only as a tryptophan synthetase mimic but as a mimic enzyme for chiral amino acid synthesis, has almost been completed, thanks to the cooperation extended by Tabushi (Figure 7, Table 2). In this study, L-amino acids could be stereospecifically synthesized, under mild conditions, from keto acids whose side chains (phenyl group, indole group, etc.) were able to fit beta-CD's internal hole. In this reaction, ethylenediamine, which was introduced into the pyranose ring (adjacent to the pyranose ring into which a pyridoxamine group had been introduced), was said to play a key role.

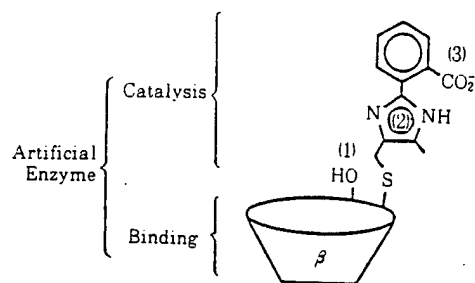


Figure 6. A Mimic of Chymotrypsin

Nos 1, 2, and 3 indicate catalytic sites.

Table 1. Comparison Between Natural Chymotrypsin and a Synthetic Chymotrypsin

ENZYME	SUBSTRATE	pH	$K_{cat} \times 10^{-2}$ ( $\text{sec}^{-1}$ )	$K_m \times 10^{-5}$ (M)
Chymotrypsin <sup>a</sup>	<i>p</i> -nitrophenyl acetate	8.0	1.1	4.0
Artificial Chymotrypsin <sup>b</sup>	<i>m</i> - <i>t</i> -butylphenyl acetate	10.7	2.8	13.3

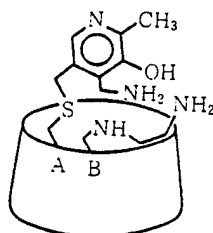


Figure 7. A Mimic of Vitamin-B<sub>6</sub>-Dependent Enzymes Obtained by Incorporating Pyridoxamine and Ethylenediamine Groups Into CD

Table 2. Chiral Amino Acid Synthesis Using a Pyridoxal-CD Enzyme Model

R-COCO <sub>2</sub> H	L : D
R = PhCH <sub>2</sub>	98/2
	95/5
Ph	98/2

On the other hand, Komiyama produced a high-molecular-weight CD by means of cross-linking; in this way, they succeeded in quantitative paraposition carboxylation and formulation of phenol rings (Figure 8, Table 3). This



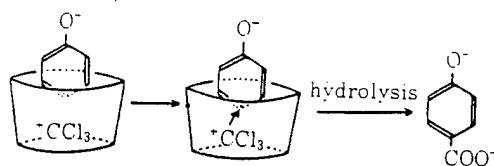


Figure 8. Site-Specific Synthetic Reaction of 4-Hydroxybenzoic Acid Using Beta-CD

Table 3. Production of 4-Hydroxybenzoic Acid Using High-Molecular-Weight Beta-CD I, II, and III contain epichlorohydrin (a crosslinking agent) at a molar ratio (to CD) of 5.7, 3.3, and 1.2, respectively.

Immobilized $\beta$ -CyD catalyst	Yield (mole%)		Selectivity for 4-hydroxybenzoic acid (%)
	4-hydroxy- benzoic acid	2-hydroxy- benzoic acid	
I	82	0	100
II	89	0	100
III	96	0	100

compound is noteworthy as a catalyst which can regulate the direction of a reagent's response and enable selective reactions. Polymerization allows easy separation of reaction products from the catalyst, thus allowing the catalyst to be repeatedly used.

## (2) Synthetic Enzymes Using Clathrate Compounds Other Than CD

Also using clathrate compounds other than CD, studies on enzyme-analogous functions have been carried out.

Breslow studied large ring compounds of water soluble type cyclophane which include pyridoxamine in their structure. Cram intensely studied imidazole-bearing cyclophane as a mimic for transacylase of L-phenyl p-nitrophenyl ester (Figure 9). Koga of the Tokyo University utilized thiol-bearing crown ether in their synthesis of oligopeptides by means of repeated thiolysis and aminolysis (Figures 10 and 11). Kellogg reported a synthetic enzyme highly capable of effecting chiral induction; this enzyme mimic was obtained by the incorporation of amino acids and nicotinamide groups into the crown ether (Figure 12). Additionally, a study on photoresponsive crown ether by Shinkai of Nagasaki University is noteworthy from the viewpoint of enzyme function regulation. When photoisomerized, some molecules showed a butterfly action and acquired an ion selectivity; further, photoisomerization caused a change in the affinity of  $K^+$  ion molecules due to the tail-biting function. Using this photoisomerization effect, a membrane for active transport of  $K^+$  has been developed (Figure 13).

Clathrate compounds, having a stereo-distinguishing capacity, are directly applicable to separation of materials. Diacetylene-type compounds, first studied by Toda of Ehime University, have been attracting attention as optical

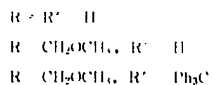
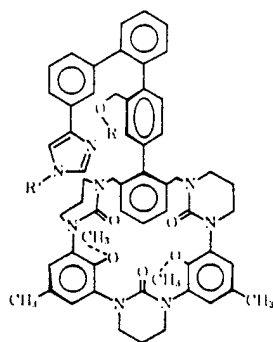


Figure 9. Imidazole-Bearing Cyclophane  
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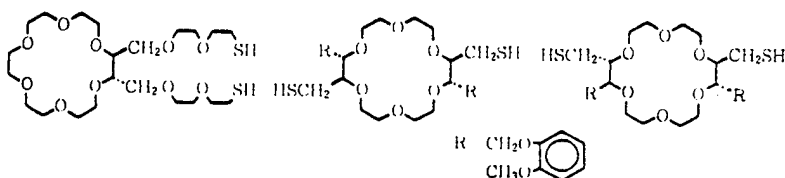


Figure 10. Thiol-Bearing Crown Ether

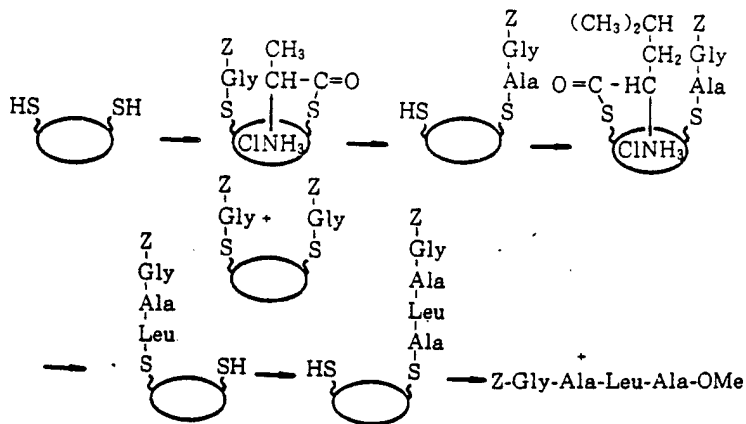
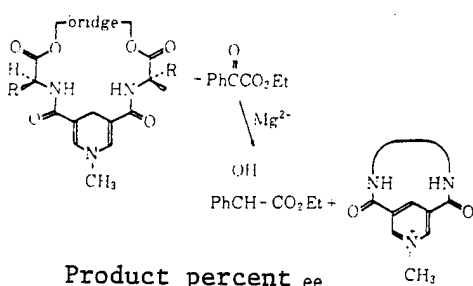


Figure 11. Oligopeptide Synthesis Using Thiol-Bearing Crown Ether



	Product percent ee
$-(\text{CH}_2)_2\text{O}(\text{CH}_2)_2-$	86 (S)
$-(\text{CH}_2)_5-$	90 (S)
$-(\text{CH}_2)_8-$	83 (S)
$m\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2-$	86 (S)

Figure 12. A Mimic of Chiral Induction Reductase Obtained Using a Large-Ring Compound

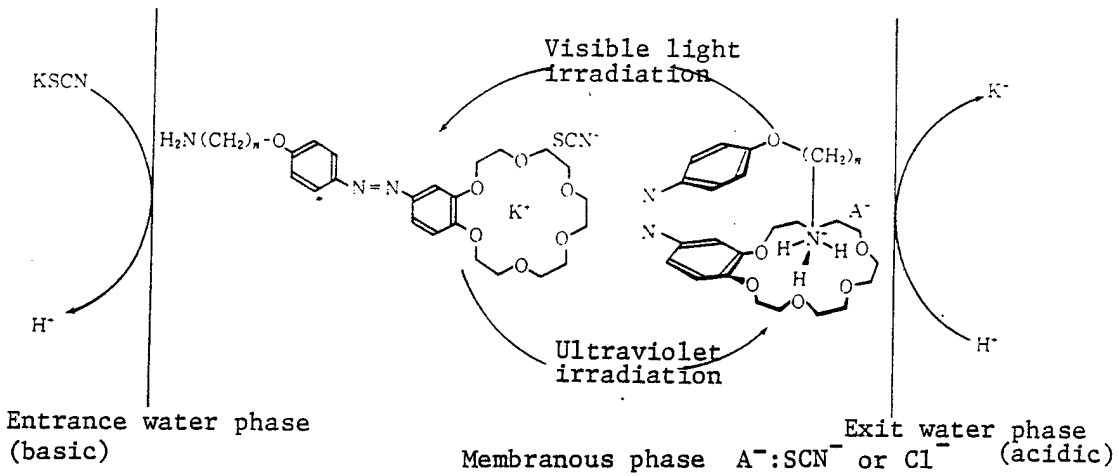


Figure 13. Optical Active Transport of  $\text{K}^+$  Ions Using Photoresponsive Crown Ether of Tail Biting Type

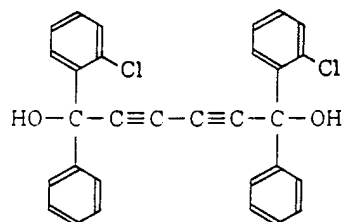


Figure 14. A New Optical Separating Agent

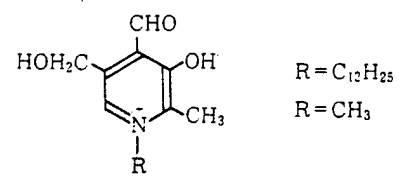


Figure 15. A Pyridoxal Model

separating agents because they asymmetrically precipitate together with prostaglandin precursors (Figure 14).

### 3.5 Synthetic Enzymes Using Micelle-Forming Molecules

Ogaka of the National Chemical Laboratory for Industry reported ester hydrolysis using cationic micelles and phenyl borate. Pyridoxal-linked micelles were useful for amino group transfer and beta-elimination of amino acids (Figure 15). Kuroki of Osaka Prefectural University reported a hydrolase model using micelles which contained imidazole and hydroxyl groups. Kamioka (Kumamoto Institute of Technology) and Murakami (Kyushu University) reported that an oligopeptide, acting as an enzyme, formed hexyl and micelle systems, which almost completed asymmetric selective hydrolysis of amino acid-containing substrates (Figure 16). Further, in a hydrolase model system having a large frequency of turnover, Menger utilized dodecyldimethylformylmethylammonium ions for the hydrolysis of phosphate esters.

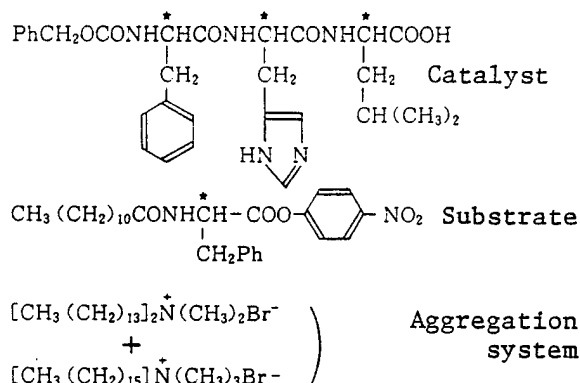


Figure 16. Composition of an Aggregation System for Chiral Selective Hydrolysis

### 3.6 Enzyme Analogues Using Organic Low-Molecular-Weight Compounds

Until now, enzyme-analogous reactions have been studied by many investigators, using enzyme-analogous organic molecules which were developed utilizing partial structures of the enzyme's active site. In the first place, this kind of study is an effective approach to enzyme reaction mechanism clarification from the organic reaction viewpoint, as has been exhibited by Bruice and Benkovic. In the second place, accumulation of data from this kind of study leads to the creation of new concepts in organic chemistry, e.g., asymmetric reactions and regulatory reactions.

Ohno of Kyoto University collected findings regarding NAD(P)-NAD(P)H models. In recent years, these investigators have been carrying out extensive research including studies of model compound substituent influences and reaction intermediates. They have also been studying the thiol-group-substituted imidazole as a protein hydrolase model.

### 3.7 Synthetic Enzymes for DNA Strand Scission

A group of antibiotics, including bleomycin, can be regarded as enzyme models which have a DNA binding site and a catalytic site for DNA strand scission. For the purpose of developing synthetic restriction enzymes and anticancer agents, new molecules having a sequence-specific DNA cleaving function have been designed and synthesized.

Dervan synthesized distamycin analogue-EDTA-Fe(II) and discovered a general rule that amid group  $m$  pieces recognize  $m+1$  pieces of adenine-thymine rich sequence of double-helical DNA (Figure 17). Furthermore, it has been disclosed that N-bromoacetyl distamycin is more specific; namely it recognizes and cuts only one of the 167 base pairs of pBR 372 plasmid (Figure 18).

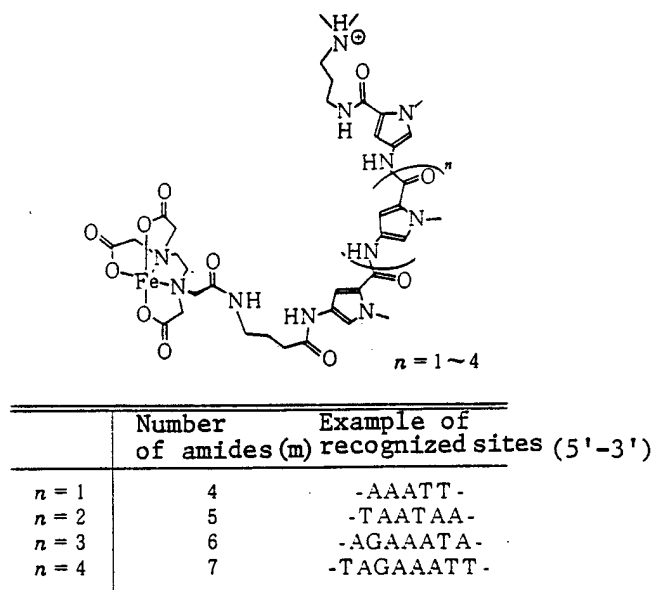


Figure 17. Sites Recognized by Oligopeptide-EDTA

On the other hand, Hecht studied DNA strand scission from a functional viewpoint. They synthesized a catalytic-site analogue of bleomycin (Figure 19) and added  $O_2$  and Fe to it for oxidation, finding that its reaction behavior is similar to that of cytochrome P-450.

### 3.8 Enzyme Models Using Metal Porphyrin

As model compounds of an oxidizing enzyme cytochrome P-450, a system consisting of a picket fence (tetraphenyl-substituted) porphyrin-metal complex, imidazole and enzymes is known. Tabushi succeeded in the epoxidation of olefin and the hydroxylation of the paraffin and aromatic ring, using Mn ions and an  $H_2$ -colloidPt system (a proton source) (Table 4). This system could be recycled more than 300 times, accelerating O-O cleavage by a factor  $10^7$  (Figure 20). This compound possesses sufficient function as a catalytic-site

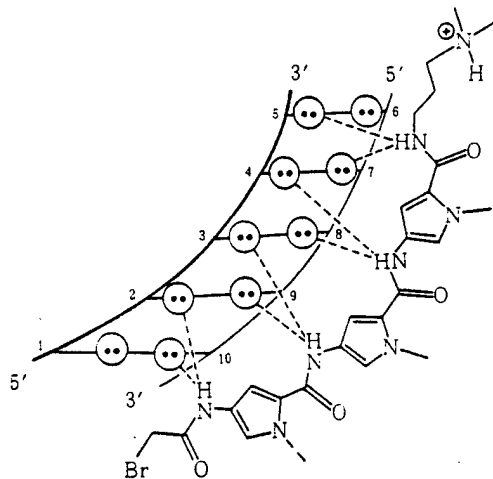


Figure 18. A Structural Model of the N-bromoreacetyldistamycin Bound to Right-Handed B DNA

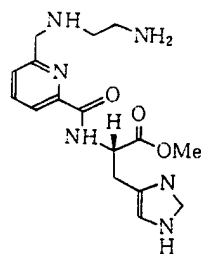


Figure 19. A Catalytic Site Model for Bleomycin

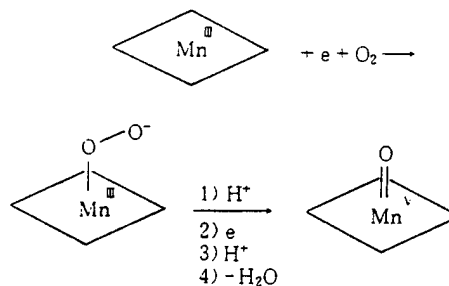


Figure 20. Formation of Porphyrin-Manganese-Oxene

Table 4. Oxidation Catalyzed by a Synthetic Cytochrome P-450

Starting compound	Product
$\begin{array}{c} R_1 \quad R_3 \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ R_2 \quad R_4 \end{array}$	$\begin{array}{c} R_1 \quad O \quad R_3 \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ R_2 \quad R_4 \end{array}$
$\begin{array}{c} R_1-CH_2-C(R_2)(R_3)-R_4 \\ \diagup \quad \diagdown \\ R_1 \quad R_4 \end{array}$	$\begin{array}{c} R_1-CH(R_2)-C(R_3)(R_4)-R_4 \\ \diagup \quad \diagdown \\ R_1 \quad R_4 \end{array}$
$R_1-H$	$R_1-OH$
$\begin{array}{c} \text{X} \\   \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} \text{X} \\   \\ \text{C}_6\text{H}_4-OH \end{array}$
$R_1 R_2 NCH_2 R_3$	$R_1 R_2 NH, R_1 R_2 NC-R_3 (R_1 R_2 NCH R_3)$

Only in initial phase

model. If an inclusion effect, which enables incorporation of substrates, is additionally given to this compound, it will acquire substrate-specificity. Therefore, this compound is promising.

#### 4. Perspective of Industrial Use of Synthetic Enzymes

As stated above, enzyme-analogous behavior has been studied from many approaches; the possibility of its industrial utilization is large. So that synthetic enzymes can surpass natural enzymes in terms of cost for production of important materials, synthetic enzymes need to have sufficiently high specificity, stability, and productivity. Further, so that synthetic enzymes can extensively and flexibly satisfy industrial needs, they must have wide applicability.

From the viewpoint of industrial use, research on synthetic enzymes is still in an initial phase. Those that are now closest to commercialization are:

1) site-selective reaction using high-molecular-weight cyclodextrin, 2) functional crown ether, and 3) coenzyme immobilization. If selectivity is improved, cytochrome P-450 models may be utilized in petrochemical industry as catalysts for the production of olefin derivatives. This is quite interesting, when we compare it with the shitasu process.

Research on synthetic restriction enzymes will not only be utilized for genetic engineering, but will largely affect designing new anticancer agents. Furthermore, it is expected that their incorporation will be utilized in packing materials, separating agents or optical separating agents for affinity chromatography.

One of the future research themes of synthetic enzymes is the development of molecular systems which are: equipped with high-level enzyme functions, easy to synthesize, highly durable, and widely applicable.

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## ELECTRONICS

### RECOVERY OF SEMICONDUCTOR INDUSTRY ASSESSED

Tokyo TOSHI KEIZAI in Japanese No 7, 1986 pp 24-27

[Report on interview with Tomihiro Matsumura, managing director of NEC; Juzo Hata, executive director of Hitachi, Ltd., and Kinichi Kadono, managing director of Toshiba: "Is the Recovery of the Semiconductor Industry Real? Interview With Executives of Three Major Manufacturers"; date and place not specified]

[Text] Newspapers are reporting on the recovery of the demand for semiconductors everyday. But judging from March's settlement of accounts, many of the relevant companies seem to anticipate a decline in their profits in the current term for the second consecutive time.

For example, the three major semiconductor manufacturers, namely, NEC, Hitachi, and Toshiba, anticipate a continued decline in their ordinary profits by 21 percent, 18 percent, and 19 percent, respectively, according to their business projections for the current term.

Then, when will semiconductors become the driving force of their business again? The general view is that it is obvious the industry is heading toward a recovery.

An interview was held with the top managers of the semiconductor departments of the three major manufacturers to ask their frank views of the current semiconductor industry. The interviewees were Tomihiro Matsumura, managing director of NEC, Juzo Hata, executive director of Hitachi, and Kinichi Kadono, managing director of Toshiba (who was informally appointed executive director after a general assembly held at the end of June).

In Terms of Volume, Semiconductor Industry Will Almost Recover to Past Peak Level This Fiscal Year

Question: Could you explain the situation of your semiconductor department in figures?

Hata: Our company's semiconductors sales were ¥540 billion in FY 1984, a 50 percent increase from a year earlier. However, the sales in FY 1985 totaled ¥390 billion, a 28-percent drop over the previous year. But the sales bottomed out in the quarter from October to December of last year, and have

been recovering at a slow pace. The sales in FY 1986 are projected at ¥430 billion, a 10-percent increase from a year ago. We expect a strong recovery in the next fiscal year which will bring about a 20 to 30-percent increase. We expect a recovery because the development of new products is progressing, and the United States will come out of its computer slump.

Kadono: Regarding the shift in the sales volume of semiconductors, total sales in FY 1984 stood at ¥435 billion, and those in FY 1985 were ¥360 billion, decreasing by 17 percent. Our sales of semiconductors are relatively well balanced among discrete products such as transistors (30 percent), bipolar ICs (21 percent), memory chips (18-19 percent), and logic ICs (29 percent). As our percentage of memory chips, whose business was stagnant last year, was lower than that of other companies, our company received less influence from the stagnation. In quantitative terms, sales have been recovering so rapidly since January that the current sales volume is as high as the record level marked in September 1984.

We expect sales for FY 1986 to total ¥435 billion, reaching the FY 1984 level.

Matsumura: Sales of semiconductors in FY 1985 were ¥450 billion, or a 24-percent decrease. Although business is still sluggish in the first half of the current fiscal year of 1986, we expect a strong recovery in the latter half, and we think it possible to chalk up a 20-percent increase for the year from FY 1985.

#### Memory Chips in Slight Shortage Due to the Recovery of the Industry

Question: Then, what kind of items or products are recovering?

Matsumura: Memory chips, whose sluggishness was the main cause of the slump in the industry, are recovering. In fact, our company produced 10 million 256K units in April. Microfiches and gate arrays also show a favorable tendency. With regard to memory chips for consumer products, new products related to VTRs and CDs are making a good showing. CCD sensors for VHS-C cassettes are selling at a pace of 60,000 units per month.

Hata: MOS memory chips for microcomputers are picking up. Our company's monthly production of 256K DRAM's [dynamic random access memory] stands at 9 million. Some of our clients are complaining about a shortage of the products, but we have to exercise prudence in production expansion. Apart from this, the demand for memory chips for VTR's, floppy disks, and automobile parts is ballooning amid the rapid progress in car electronics technology.

Kadono: Among others, the demand for bipolar IC's and discrete products such as transistors and diodes have picked up, driven by exports to Southeast Asian countries. This is partly due to Japanese manufacturers shifting their production overseas, in view of the strong yen, and partly due to the expanded production of TVs and VTRs for export by NICs (newly industrialized countries), including Korea, Taiwan, Singapore, and Malaysia, through increased competition. Accordingly, the normal level of production of these items have fully recovered. However, U.S.-oriented exports and domestic sales are still

Basic Trend of the Three Major Semiconductor Manufacturers

(Unit: ¥100 million; yen)

	NEC Corp.	Hitachi, Ltd.	Toshiba Corp.
Sales amount	18,893.4 19,705.0 22,000.0	30,257.5 30,033.9 29,000.0	25,259.5 25,195.6 27,200.0
Ordinary profits	1,259.0 945.2 750.0	2,559.1 1,580.4 1,300.0	1,440.3 804.6 650.0
Net profits	511.0 530.2 400.0	1,054.1 880.4 720.0	665.3 540.6 325.0
Profit per share	37.2 38.2 28.8	37.6 31.4 25.7	24.5 20.2 12.1
Dividend per share	8.5 9.0 9.0	9.0 9.0 9.0	8.0 8.0 8.0
Sales amount of semicon- ductor	5,900 4,500 5,200	5,400 3,900 4,300	4,350 3,600 4,350

Note: Upper number=the third quarter of 1985; middle number=the third quarter of 1986; lower number=projection for the third quarter of 1987.

stagnant. Domestic clients are wary of production expansion because of the strong yen.

Development of New Products and Shift of Production Overseas Are Counter-measures Against the Strong Yen

Question: In terms of quantity, production has almost recovered to the second level of FY 1984. Prices, however, show slow recovery. In this respect, do you think it will take some more time for profitability to be restored?

Hata: As the manufacturers of 256Ks are cautious of production increases, there is a slight shortage in products, and therefore, a depreciation of prices cannot take place. In fact, the prices are being raised. At the moment the unit price is ¥320 to ¥390, but our company intends to raise it to ¥400. In the American market, however, cheap memory chips made in Korea made inroads, taking advantage of the Japanese products' loss of their competitive edge due to dumping duties. We should not take an optimistic view of the market.

Kadono, Matsumura: As far as the semiconductor business is concerned, the expansion of production volume boosts profits, even if prices do not recover.

Question: While the market recovery is slow, the yen appreciates at a fast pace. Can profits be secured under the exchange rate of ¥160 to the dollar?

Hata: Our company is attempting to streamline itself and reduce costs in an effort to counter the strong yen. But these will not be enough under the exchange rate of ¥160 to the dollar. Therefore, developing new high value-added products by making the most of state-of-the-art technology is a priority. In other words, it is important to lower the ratio of general purpose products, such as memory chips, and raise the ratio of custom-made products. New products would have a competitive edge even under the exchange rate of ¥160 to the dollar. Our company's ratio of memory chips has declined to about 30 percent.

Concerning exports, our company tries to produce them in the dollar-linked areas. Hitachi owns semiconductor plants in the United States, European countries, and Malaysia. We intend to boost the production in these plants. All of the plants used to be assembly plants using chips transported from Japan. But in the plant in the United States, we plan to produce the chips and assemble the products. Regarding revenues, all I can say at the moment is that the situation is better now than last year.

Matsumura: The only means of securing revenues is to raise the ratio of new products. While the new product ratio in the latter half of FY 1985 stood at 20 percent, NEC aims at 30 percent in FY 1986. The ratio of memory chips during the peak period was 32 to 33 percent, but it has now sunk below 30 percent.

With regard to measures to counter the strong yen, NEC's U.S.-oriented export ratio was lowered to 7-8 percent, although the figure used to hover at about 15 percent during the peak period. Europe-oriented exports account for 25 percent, most of which are based on the mark. As a future step, we have to shift to local production. NEC already has a plant in the United States that handles everything from chips to the finished product. The plant is now in its second phase of expansion. In the American market, our company would sustain little impact from the strong yen because most of the goods are produced and sold in dollars. So our concern is rather with NICs. Other than the plant in the United States, NEC has a plant in Singapore and a knockdown factory in Malaysia, and one is under construction in Scotland, which is slated to be completed next spring.

Kadono: Even under the exchange rate of ¥160 to the dollar, Toshiba could mark up the prices of products produced only in Japan and still manage. Basically, however, we have to shift production to overseas. Toshiba's Malaysia Plant has been manufacturing transistors, but our company intends to bring chips and assemble them there, with a view to producing memory chips also. At the same time, we plan to double the production of 256Ks at our plant in West Germany, which is currently producing 1 million to 2 million units per month. Our plant in the United States has been specializing in 64K assembly. But now a small quantity of 256Ks are being produced on a trial basis, with a plan to mass produce 256Ks in the future. We will wait and see until the trade friction subsides.

## Investments Declining

Question: Will the recovery in terms of quantity lead to the recovery of equipment investments?

Kadono: Toshiba's investments in FY 1985 amounted to ¥90 billion. But we decided to reduce investments in FY 1986 to about ¥75 billion. Most of them are for developing new products and increasing the production of 1M chips.

Hata: In FY 1985, we invested ¥90 billion as a group, and Hitachi itself invested ¥60 billion, a 30-percent decrease over FY 1984. In FY 1988, investments of the group and the company itself will be reduced by as much as 33 percent to ¥60 billion and ¥40 billion, respectively.

Matsumura: NEC invested ¥100 billion last year, but we plan to cut back on our investments by 30 percent to ¥70 billion.

Question: How are you going to cope with the forthcoming era of 1M chips?

Kadono: Toshiba has already achieved a monthly production volume of 200,000 to 300,000 units. The main users are minicomputer manufacturers. It is said that IBM has started production of 1M chips for its own mainframe computers. In this context, I expect the demand for 1M chips for mainframe computers will be created in Japan as well in the future. I suppose FY 1987 will certainly be the era of 1M chips, which should begin in the latter half of FY 1986.

Matsumura: The 1M chip is still in the phase of trial production with a monthly output of tens of thousands of units. The advent of the 1M chip era should take at least another 2 years. NEC's attitude toward this field is to wait until a worldwide standard is set and have a second runner commercial strategy.

Hata: Our 1M DRAM is in the phase of sample shipments with a monthly production of tens of thousands of units. I imagine the era of 1M chips will begin in the latter half of next year at the earliest. The merits of acquiring the technology of 1M chips are ample when we consider the possibility of applying it to the ultraprecision technology of microcomputers and logic ICs.

Question: It has been reported that the U.S.-Japan semiconductor negotiations reached a tentative accord in top level talks between U.S. Trade Representative Yeutter and Japan's International Trade and Industry Minister Watanabe. Could you comment on this and set forth your measures for the future?

Matsumura: In my opinion, U.S.-Japan semiconductor friction should not arise. The reason is that of the estimated \$50 billion U.S.-Japan trade imbalance, the semiconductor trade imbalance accounts for about ¥100 billion (exports: ¥200 billion, imports: ¥100 billion), or a mere 1 percent. Notwithstanding this, semiconductors are regarded as a major subject of U.S.-Japan trade friction second to automobiles.

The problem is not so much trade friction as a technological gap which can be dubbed "industrial policy friction" caused by the impatience of American manufacturers.

As countermeasures, NEC already dropped its U.S.-oriented export ratio to 7-8 percent on a consolidated basis, and began the entire production of semiconductors at our plant in the United States. Therefore, the astoundingly high dumping duty of 108 percent has had little impact on our 256Ks.

Actually, I think NEC is the largest buyer of American semiconductors in the world. We purchase nearly everything, except for the items we manufacture ourselves, from the United States. Chief executives of American semiconductor manufacturers often visit NEC and say "thank you, thank you."

Hata: The main problems are the American manufacturers' access to the Japanese market and the prices.

The problem of prices is a sensitive issue because simultaneous markups by major manufacturers would involve the Antitrust Law and meet resistance from major users. A provisional decision on the 256K, our main product, was handed down in the United States, and as a result, a 19.8 percent dumping duty is to be levied on our 256K products. We have to exercise prudence for the time-being. Hitachi is the largest exporter of semiconductors, but exports in FY 1986 are likely to decline further.

Regarding access to the Japanese market, Hitachi is also making efforts to address the problem, and purchases as many American semiconductors as possible. We even try to buy items we are producing if the prices are about the same. Roughly speaking, half of our semiconductors are for industrial use and the remaining for consumer products. As Japanese consumer products are overwhelmingly competitive, many of the semiconductors we buy from the United States are for industrial use.

Kadono: A provisional decision on our 256K imposed a dumping duty of 49.5 percent, which is a middle rate compared to the other rates imposed on the three major manufacturers. It is hard for us to understand why there is so much variance in duty rates. Judging from the estimation of the costs based on data submitted by manufacturers, I know that two main considerations are whether the market prices in the United States are below costs and whether they are below the market prices in Japan. But there should not be such large differences among the manufacturers.

The prices with dumping duties added onto them do not meet the market situation. Besides, the interests of Japanese semiconductor manufacturers conflict with those of users in the United States.

While shifting production to the United States, Toshiba will concentrate its sales effort on custom-made products rather than on general purpose products, thus accommodating diverse requirements. For instance, we will establish designing centers in various locations throughout the world (currently, Toshiba has three designing centers in the United States and one in West

Germany), with a view to expanding our ASIC (custom IC) field. By connecting terminal computers in those centers with a communication satellite, we can develop a system that can immediately meet the needs of our users after a design is transmitted.

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## LASER TECHNOLOGY

### DEVELOPMENT, APPLICATION OF SOLID STATE LASER MATERIAL DISCUSSED

Tokyo OPTRONICS in Japanese Jun 86 pp 87-91

[Article by Yoshimasa Fujii, member of the Electronic Material Research Institute of Sumitomo Metal Mining Co., Ltd.: "Current State of Development of Solid Laser Materials and Their Application; Review of New Laser Trends, Possibility of Various Applications"]

#### [Excerpts] 1. Introduction

In the 26 years since the invention of the laser, a large number of technologies have been built up in connection with solid lasers, which began with the ruby laser. There is a saying that some technologies requiring a long development stage achieve a high degree of growth; this must be the case with solid lasers which, at last, see their full-fledged application beginning.

Figure 1 shows the world trend of demand for solid lasers, prepared from a list printed in the January issue of LASER FOCUS. The solid laser last year showed a fine, steady annual growth of 24 percent, in spite of the troubled economy, which included a semiconductor recession. Military demands account for a major part of the world demand. Applications in lasermachining and in medicine are growing rapidly, with their combined totals about to exceed 50 percent of the grand total which amounts to \$190 million or approximately 8,000 machines. This tendency for growth is deep-seated and expected to go on at an annual rate of 30 percent or more in the coming years with laser machining and laser medicine dominating the growth.

This nation has seen the rapid expansion of the application of lasers in machining and medicine, particularly in semiconductor processing. According to the Optoelectronic Industry and Technology Development Association (OITDA), the relevant production was ¥3.9 billion for FY 1984 and is predicted to be ¥4.8 billion in FY 1985. This is a 24 percent increase. With a steady recovery of the semiconductor industry predicted, this year may see further expansion in demand.

Solid lasers are compact in size, high in output, strong mechanically, and superior in durability; they are amenable to repeated use and capable of good control of light, e.g., emission of short pulses. Because of their short wavelengths, compared with those of carbon dioxide gas lasers, solid lasers permit good concentrations of light and even use of optical fibers. These

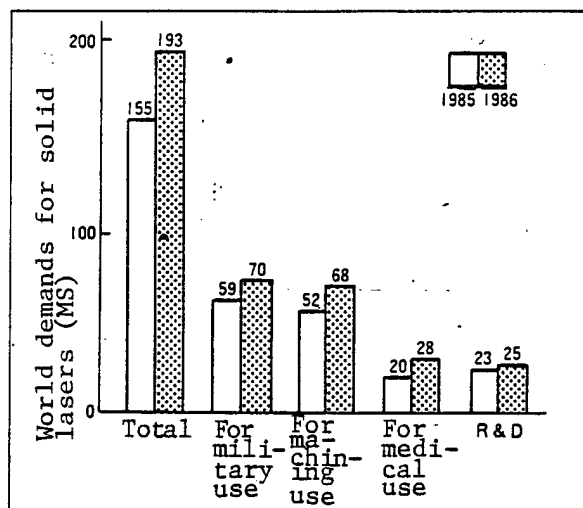


Figure 1. World Trend for Demand of Solid Lasers

features of solid lasers are of overriding significance in industrial lasers and bode well for their future growth. The relevant technology of the nation, in turn, is the best in the world, and corporations are going to take their share of the world market. With the growing of YAG ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) crystals and the processing of laser rods beginning for domestic production, though belatedly, the development of laser systems seems to be underway. Once the apparatus for laser beams was regarded as expensive and as requiring special technologies; however, with the general use of lasers, and with their incorporation in robot systems, the beam has become a credible instrument which anyone can manipulate with ease. Lasers are finding uses also in machine tools which are conveniently available even to small- and medium-sized enterprises.

This is the background of requirements for solid lasers. Recently, there has been increased demand for the development of a solid laser with higher efficiency and higher output so that the area of application for solid lasers can be further expanded and the pace accelerated. The R&D of relevant new crystal materials, hence, has been revived and is gathering force. The currently available YAG laser uses  $\text{ND}^{3+}$  ions as its activated ion and involves a near-infrared ray with a wavelength of  $1.064 \mu\text{m}$ , exclusively. Laser materials which permit emission of beams with a wavelength other than this, therefore, are in demand, e.g., beams in the ultraviolet, visible, and intermediate-infrared regions. Furthermore, momentum is gathering on R&D of a tunable solid laser, i.e., a solid laser capable of emitting laser beams the wavelength of which can be varied continuously in a frequency spectrum.

Though this paper deals primarily with laser crystals which have recently achieved remarkable advances, it should be noted that R&D of high-capacity glass lasers and color-center lasers of variable frequencies is also pushing on steadfastly.

## 2. Present State of Development of YAG Crystals

Since approximately 98 percent of solid lasers are made of YAG, YAG crystals may not properly be termed a new laser material. However, with domestic production of YAG crystals for commercial purposes having begun recently, and with competition for the development of a larger, higher quality crystal getting more intense, the conventional YAG crystals are undergoing a transformation. Whereas, in the past, all of the crystals were imported and hence the stability of supply and quality not ensured, a substantial portion of the crystals used here are presently being produced domestically. Laser rods with a diameter of 10 mm and a length of 150 mm, which were hard to obtain in the past, are becoming available in increasing amounts and their price is going down, thereby accelerating their general use.

Technology for growing the crystals is also progressing, and is reflected in an increase in diameter from 40 mm to 60 mm and, further, to 3 inches. The control of the core through control of the temperature distribution requires sophisticated technologies. Efforts are also being made to reduce the color center by means of stepping up the purity of the raw material and to diminish striation by rendering the temperature control more precise; this with a view to turning out a product of improved quality. Research is continuing in the following areas: the automation of the processes of pulling out the crystals and the processing of its side surface, a mass production process in connection with the processing of the end surface, technologies for assessing the precision in processing; those of assessing the optical homogeneity of the product, and those of assessing the dynamic characteristics of laser beams. The development of AR coating, which has a high resistance to light, has also advanced notably in recent years.

The final assessment of laser rods, which must be set up as a system, is made with respect to the output or power of the rod, the angle of spread of the rod, and its homogeneity, among other things. The correlation of the ultimate assessment to the process of producing laser rods is an important key to the stabilization of the quality of the product. In general, however, the concentration of the activated ion,  $\text{Nd}^{3+}$ , constitutes the most important parameter, which seems to have to be controlled within a narrower range than the conventional  $\pm 0.1$  percent.

A power capacity of 565 watts has recently been obtained from one single ND: YAG laser system, and higher capacities are expected soon. Figure 2 [omitted] shows a typical YAG crystal. Figure 3 shows the input-output curves for lasers.

## 3. Development of Laser Materials of High Output and High Efficiency

With the efficiency of YAG lasers currently limited to 2-3 percent, improvement is in serious demand. This implies that 97-98 percent of the input excitation energy is eventually dissipated as thermal energy without being used as laser output. Should efficiency triple, the capacity of the supply source can be reduced to one-third as can the cooling system, leading to the extension of the life of the lamp and conceivably to the improvement of the stability of the

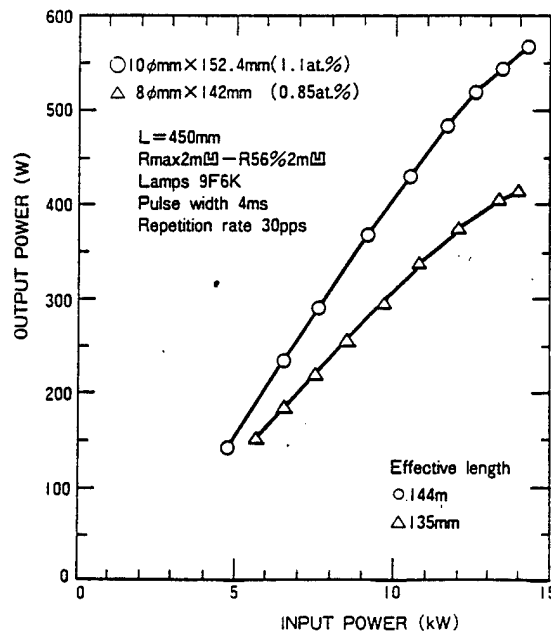


Figure 3. Input-Output Characteristics of the Nd<sup>3+</sup>:YAG Laser Rod

laser. The major reason for low efficiency is this; the absorption spectrum of the activated ND<sup>3+</sup> ion is a very narrow line spectrum and the light-emitting spectra of Xe and Kr are very wide band spectra. Incorporation of a sensitizing object having a wide absorption spectrum, therefore, may conceivably lend itself to removing this bottleneck. Though research on the mechanism of sensitization by resonance energy transfer has been going on for a long time, the addition of redundant impurities may adversely affect the crystal by causing quality deterioration and difficulties in growth. It was found recently, however, that a GSGG (Gd<sub>3</sub>Sc<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>) crystal, to which Nd and Cr are added, achieves an efficiency approximately three times that of Nd:YAG. Active R&D on this subject, therefore, has revived.

The absorption spectrum of the ion Cr<sup>3+</sup> forms a wide band and hence utilizes the lamplight efficiently. While the Cr<sup>3+</sup> ion is affected in large measure by the relevant crystallization field, the garnet crystal is capable of freely altering its field by having its constituent elements replaced by various ions of rare earth elements, etc., of different diameters. It is, therefore, possible to induce an effective resonance energy transfer by adjusting the light emission spectrum of the Cr<sup>3+</sup> ion to correspond to the light absorption spectrum of Nd<sup>3+</sup>. The GSGG crystal is hardly capable of stoichiometric growth and is subject to color-center formation; the GSAG crystal (Gd<sub>3</sub>Sc<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>) in which Ga of the GSGG is replaced with Al has been, hence, spotlighted. Though difficulties in obtaining the Sc material have been talked about, its price is currently stable with a recent substantial change in the situation.

The Nd:GGG (Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>) crystal exhibits many superior characteristics as a laser material and is a prospective material for high output laser emission.

Because of a high segregation coefficient in  $\text{Nd}^{3+}$ , high-quality crystals, i.e., of large size (diameter 80 mm and length 300 mm) with a high concentration (up to 4 atomic percent) are possible at a rapid growth rate. Because of the lack of a core area where distortions concentrate, large laser slabs are also possible. Since the advantages of Nd:GGG laser materials come from the use of neodymium in high concentration, the problem of thermal lens effects is generally involved. The material, therefore, is adapted to lasers with pulse excited high output rods and those of the slab type; it is also possible to increase output of inserting an Nd:GGG crystal and a solarization preventing pipe filter into a pulse excited YAG-laser apparatus. Figure 4 [omitted] shows Nd:GGGs, laser rods, and laser slabs and Figure 5 shows a comparison between laser characteristics of YAG and GGG crystals. Relevant Nd concentrations are 1 atomic percent and 2 atomic percent, respectively, and a rise in output of approximately 20 percent is seen for the higher concentration. Lasers of the slab type exhibit a light path following a zigzag course due to the total reflection. This allows the evening out of the variation of refractive index and effects of double refraction occurring in the direction of slab thickness. Slab type lasers also permit application of excitation and cooling in the large areas of their upper and lower surfaces. This implies that the slab type lasers are possible on a large scale and, therefore, developmental research is being pushed aimed at a solid laser in the kilowatt class. The Nd:GGG crystal, in turn, seems to be adapted particularly to slab lasers because the material has a heat conductance approximately 10 times that of glass and because it is available with high Nd concentrations and in large sizes. Refer to item 15 in the bibliography for listed optical characteristics and thermomechanical characteristics for various materials. Figure 6 presents the structure of a trial-manufactured slab laser. Relevant research is currently aimed at a slab of larger size, optimization of the reflection mirror pipe, improvement of the cooling system, improvement of the temperature distribution of the side and the end surfaces, and so on.

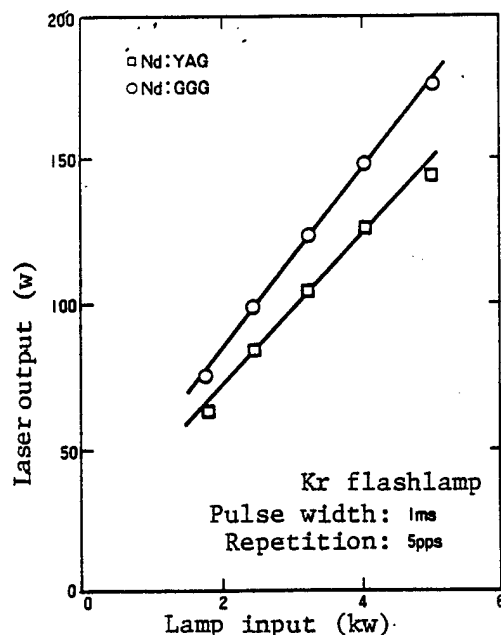


Figure 5. Comparison of the ND:YAG Laser With the Nd:GGG Laser

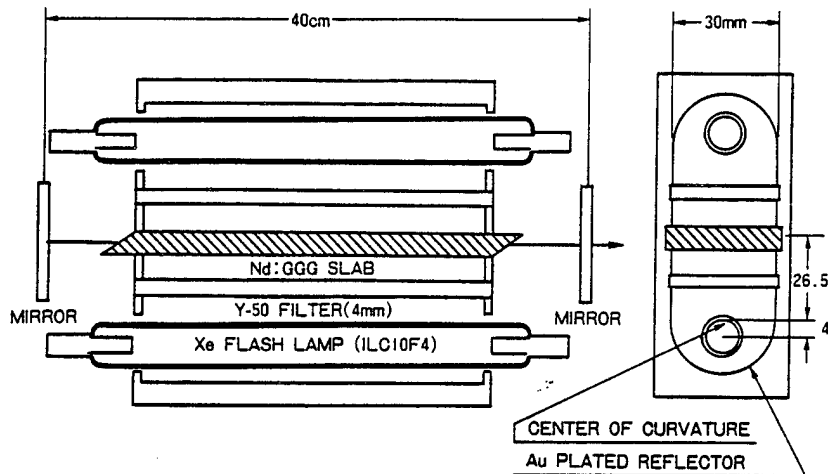


Figure 6. Structure of the  $\text{Nd}^{3+}:\text{GGG}$  Slab Laser

#### 4. Development of Materials for Solid Lasers of Variable Wavelength and of Short Wavelength

Demands for solid lasers of variable wavelength and of shorter wavelength are deeprooted, not only for the fine tooling of workpieces, but also in applications based on the selective absorption of laser beams such as in laser medicine, in laser makeup, in laser printing, and, further, in laser chemistry including separation of uranium isotopes.

Since the discovery of the emission of continuous wave lasers in the Cr:alexandrite ( $\text{BeAl}_2\text{O}_4$ ) crystal, R&D on various crystals has been reinvigorated. The energy difference between  ${}^4\text{T}_2$ - ${}^2\text{E}$  levels varies with the crystal field strength; in crystals chosen specifically for the strength of their field, the  $\text{Cr}^{3+}$  ion thermally excited from the  ${}^2\text{E}$  energy level of long life-span lends itself to a laser of variable wavelength. This is based on the transition from the  ${}^4\text{T}_2$  level to the phonon vibration level, and leads to gains in effective fluorescent lifespan and in fluorescent efficiency. Though crystals of alexandrite and emerald,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , among others, have been in the limelight, researchers are confronted with the difficulty in growing crystals of high quality and large size and with the problem of the crystals' low resistance to surrounding conditions in a practical laser because of the involvement of Be.

In the garnet crystal in contrast, the crystal field size varies easily with the substitution of its ions with a rare-earth element, etc. Garnet crystals of high quality and large size can be grown with comparative ease; GSGG, GSAG, LLGG ( $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ ), among others, have been spotlighted, and elucidation of the problems of excitation level absorption (ESA), color center, etc. are being pushed ahead. There has also been recent progress in R&D of fluoride crystals such as Cr:KznF<sub>3</sub>.

Where development of solid lasers with shorter wavelengths is concerned, development of a method in which optical second high frequency generation (SHG) materials are utilized in multiple steps is spotlighted, as is development of a method of directly emitting laser beams with a short wavelength.

Among the notable SHG crystals are, presently: organic single crystals such as MNa, KTP ( $\text{KTiOPO}_4$ ),  $\beta\text{-BaB}_2\text{O}_4$ , and Mg-doped  $\text{LiNbO}_3$ . KTP, in particular, has the bright prospect of practical application because of its high efficiency, high stability, and high resistance to damage from light.

Materials for lasers of short wavelength include Ce:YLF ( $\text{LiYF}_4$ ) and  $\text{LaF}_3$  crystals. As the wavelength of a laser shortens, its fluorescent lifespan is reduced and the emission of laser beams becomes more difficult in general. It has been reported, however, that emission of a beam with a wavelength of  $0.308\text{--}0.325\text{ }\mu\text{m}$  was produced by means of excimer laser excitation of Ce:YLF crystals. The YLF crystal is also notable in that reports have been made on the emission, at room temperature, of many laser beams ranging from the near ultraviolet to the near infrared regions by means of doping with various ions of the rare earth elements. The crystal is also notable because the effects of the change in its thermal expansion and those of the change in its refractive index, both produced by temperature changes, counteract each other by virtue of its cubic crystal form. By this means the thermal lens effect is minimized and a stable polarized beam of laser light is made possible. Currently, efforts are being exerted for the improvement of the quality and increase of the size of the crystal. Figure 7 [omitted] is a photograph of the YLF crystal.

## 5. Prospects for Practical Application

The nation has been developing material for lasers for a long time, but R&D for full-scale practical application has begun only recently. Though the nation produces YAG crystals of a quality comparable to that of imported ones, it is hoped that the quality can be improved further so the efficiency can be raised and the areas of application can be expanded. Nevertheless, the nation seems to lag considerably in the development of new materials for solid lasers other than for YAG. Both in quality and quantity, Japan is behind the United States, West Germany, and so on, which are aggressively engaged in the relevant R&D.

In connection with the raw materials for solid lasers, it is hoped that a stable supply of more highly purified materials is possible by securing the supply of rare earth elements, scandium, irridium, and fluorides, among other things, and by improving the relevant technologies for purification and analysis. It is also hoped that larger, higher-quality crystals can be produced as a result of research on the mechanism of crystal growth, improvement of technologies for the control of crystals and improvement of technologies for the assessment of the physical properties of crystals. Though it is possible to grow YAG crystals with a diameter of 3 inches and GGG crystals with a diameter of 4 inches, improvement and stabilization of the quality have yet to be achieved. Laser materials contain high concentrations of activated ions, which act as impurities in the crystal and which, hence, pose difficulties unique to the material in crystal growth.

Among the urgent problems in connection with equipment for solid lasers are: development of an excitation lamp of greater efficiency, such as an alkali-added rare-gas alumina tube lamp; development of a method for the excitation of solid lasers by means of LD and LED; development of a high precision mirror with high resistance to damage from light; development of technologies for high precision grinding of large surfaces of laser slabs, and development of slab laser cavity.

Where machines and equipment for the application of solid lasers are concerned, expansion of the application field of solid lasers is expected in the electronic industry through the development of superfine tooling and high power tooling based on solid lasers. Many developmental problems, furthermore, are expected to be resolved: demonstration of the feasibility of a flexible machining center (FMC); laser medicine and, in particular, the diagnosis and treatment of cancer; application of solid lasers to laser makeup and laser printing; laser chemistry and, in particular, development of solid lasers of variable wavelength available for uranium concentration; and application to space science and laser radar.

If these developmental problems are to be resolved, it will be necessary to push ahead intensively with R&D. The concerted efforts of manufacturers (of raw materials, equipment, and application machines), government research organs, and universities will be needed. One must also take into account international cooperation in research and technology.

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CSO: 4306/2582

## NEW MATERIALS

### METHODS OF DEALING WITH CERAMIC BRITTLENESS DISCUSSED

Tokyo CERAMICS JAPAN in Japanese Jul 86 pp 581-589

[Article by Koichi Niihara, professor of physics at the National Defense Academy: "A Special Feature--Challenge of Toughening Ceramics"]

[Text] 1. Preface

Coupled with the development of advanced technology, various oxide and nonoxide ceramics and their compounds, which drew attention as new structural materials, have been studied enthusiastically by many people throughout the world. As a result, a lot of high performance ceramics have been developed and some of them have already been put to practical use. Ceramics are, however, very brittle compared with metallic and high-molecular materials. In other words, mechanical properties of ceramics are sensitive to microfaults existing on the surface or inside of them because of low fracture energy and fracture toughness, so fractures occur with catastrophic results. They are vulnerable to mechanical and thermal impact and are hard to process. Thus, the problem is that the various properties of ceramics change depending heavily on their microstructures which are influenced by production processes. It is, therefore, indispensable that the brittleness of ceramics be improved in order to put them to wide practical use as structural materials.

There are two types of ceramic fractures: instantaneous and slow fracture. In each case fracture is caused by the growth of a microcrack existing on the surface or inside the material, as shown in Figure 1. The condition of the fracture can be shown in the following formula:

$$\sigma_t = \frac{1}{Y} \left( \frac{2 E \gamma_t}{c} \right)^{1/2} = \frac{1}{Y} \frac{K_{Ic}}{c^{1/2}} \quad (1)$$

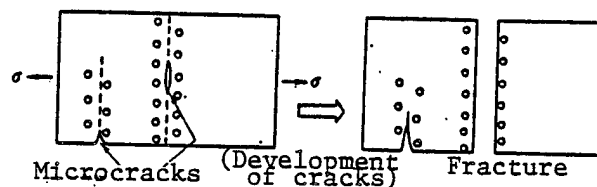


Figure 1. Fracture Caused by Growth of Microcrack

$Y$  symbolizes the form factor of a microcrack,  $E$  Young's modulus,  $\gamma_i$  fracture energy,  $c$  the size of a fracture source and  $K_{IC}$  a critical stress expansion coefficient (fracture toughness).  $K_{IC}$  is a material constant indicating the degree of the resistance of the material developing brittleness fracture to fracture. The material with a large  $K_{IC}$  can be said to be a very tough material.

The above fracture conditions were led by the supposition that a crack does not grow under lower critical stress. In fact, however, a crack grows slowly in material even under lower stress. The phenomenon of the so-called slow crack growth (SCG) can be observed. SCG occurs due to stress corrosion by water, the slide of a grain boundary, the formation of a cavity in a grain boundary and atomic diffusion, and the speed of growth can be shown in the following formula:

$$\frac{dc}{dt} = AK_I^n \quad (2)$$

$A$  and  $n$  are the constants depending on the material and environment, and  $K_I$  is a mechanical parameter ( $K_I = Y\sigma_a c^{1/2}$ ) which indicates how many times the stress which is generated at the end of a crack is larger than the external stress ( $\sigma_a$ ). Therefore, actual ceramic fracture occurs when a microcrack grows steadily in accordance with formula (2), and this grown crack satisfies formula (1), resulting in unstable growth.

Therefore, the brittleness of ceramics can be improved in terms of engineering in the following ways:

- (1) The development of a material in which a crack grows little under lower stress than fracture stress, i.e., the material of long life.
- (2) The development of a production process that can severely control the size and distribution of cracks, stomas, coarse grains, and interposed materials, all of which provide sources of cracks.
- (3) The development of prospective life forecasting technology through non-destructive tests, fracture probability, and assurance tests.
- (4) Machine designing that avoids stress concentration or ensures the generation of compressive stress.

However, when manufacturing ceramic parts of high mechanical reliability after achieving items (1) to (4),

(5) The achievement of toughening materials is very important. This is because, the improvement of toughness of ceramics produces many results as follows:

- (a) It results in strengthened ceramic materials, easy cutting, grinding, and polishing, and improved resistance to damage on the surface.

- (b) It results in reduced sensitivity of various properties to microcracks or microstructures.
- (c) Therefore, designing materials and machines becomes easy.
- (d) It results in longer life of material.
- (e) It can control the formation of a new fracture source during operation.
- (f) It reduces psychological pressure about the brittleness of ceramics.

Therefore, the fracture toughness ( $K_{IC}$ ) of ceramics must be improved even slightly. The author's view will be given as follows regarding the basic way of thinking about the toughening or the strengthening of ceramics, toughening mechanisms, and present conditions and a future outlook for this field.

## 2. Mechanisms for Toughening Ceramics

### 2.1 Basic Way of Thinking

First of all, it is necessary to understand why ceramics are brittle, when attempting to toughen ceramics or improve  $K_{IC}$ . From the viewpoint of material science, the brittleness of ceramics is attributable to 1) low dislocation density, 2) small transitional movements, 3) few slippage systems, and 4) an inadequate amount of energy for the formation and growth of cracks. More basically, however, the brittleness of ceramics is due to chemical bond; ceramics are made of very strong directional ionic bonds, different from metallic materials bonded by free electrons. On the other hand, the advantages of ceramics such as a high melting point, chemical stability, high friction- and abrasion-resistance due to hardness, creep-resistance, a high Young's modulus, a high tolerance of high temperatures, etc., are all attributable to their chemical bond. Therefore, the thesis of improving the  $K_{IC}$  of ceramics is to "improve  $K_{IC}$  without losing these excellent qualities." This means the need to "make ceramics unbrittle while leaving them as brittle as they are." In order to solve this thesis it is necessary to adopt a method either to introduce controlled stress into material and utilize it or to develop brittleness fracture in a microarea by this controlled stress and utilize it. The latter may sound like a catechism, but it is to make material unbrittle by utilizing its brittleness or to improve a defect by utilizing it. Or again, it means to improve brittleness macroscopically by generating controlled fracture in a microarea by utilizing brittleness, the defect of ceramics.

### 2.2 Toughening Mechanisms

$K_{IC}$ , the fracture toughness of ceramics, can be formulated as follows, as is clear from formula (1):

$$K_{IC} = (2 E \gamma_i)^{\frac{1}{2}} \quad (3)$$

Therefore, the material with a high Young's modulus and strong fracture energy should be developed in order to obtain ceramics with high toughness. Generally, the Young's modulus is the constant of materials insensitive to structure. Accordingly, the main object of toughening is increasing  $\gamma_i$ .  $\gamma_i$  includes absorption mechanisms of many other energies than thermal mechanical surface energy ( $\gamma_0$ ), and can be indicated by the contributions by plastic deformation ( $\gamma_p$ ), stomas ( $\gamma_{po}$ ) grain boundaries ( $\gamma_{gb}$ ), microcracks ( $\gamma_{mc}$ ), the modification of dispersed particles ( $\gamma_t$ ), etc., as shown in formula (4).

$$\gamma_i = \gamma_0 + \gamma_p + \gamma_{po} + \gamma_{gb} + \gamma_{mc} + \gamma_t + \dots \quad (4)$$

The research for toughening ceramics is to realize increased  $\gamma_i$  with actual material by discovering such energy absorption mechanisms.

The mechanisms for toughening ceramics are consolidated in Table 1. The substantial mechanism that largely contributes to increasing fracture energy is the plastic deformation at the end of a crack, as given in Item I of Table 1. This method, however, is not appropriate for ceramics except for a specific purpose as mentioned in the preceding chapter. This mechanism is generally difficult to materialize except for the case of a high temperature under which even ceramics develop plastic deformation.

Table 1. Mechanisms for Toughening Ceramics

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I.	Substantial improvement--plastic deformation
II.	Control of microstructures Stoma, particle diameter, granule shape, grain boundary, microcrack, etc.
III.	Toughness improvement by compounding
	(1) Ceramics/metallic system
	(2) Ceramics/ceramic system
	(a) Due to interaction between end of crack and dispersed phase
	• Pinning at end of crack
	• Bending at end of crack
	• Deflection and distortion at end of crack
	(b) In process zone of end of crack
	• Stress inductive modification
	• Generation of microcrack
	• Pullout of whisker and fiber

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The  $K_{IC}$  value of a polycrystal ceramic material is typically larger than that of a single crystal, as shown in Figure 2. This indicates that the course of fracture of a polycrystal is more complicated than that of a single crystal. On considering the structural differences between single crystals and polycrystals, it can naturally be found that microstructures of a crystal particle diameter, shape, stoma, grain boundary, impurity phase, microcrack, and residual stress strongly influence  $K_{IC}$ . The explanation of the improvement of  $K_{IC}$  by controlling these microstructures of ceramics will be omitted here, since it is discussed in detail by Suzuki in the special edition of this magazine.

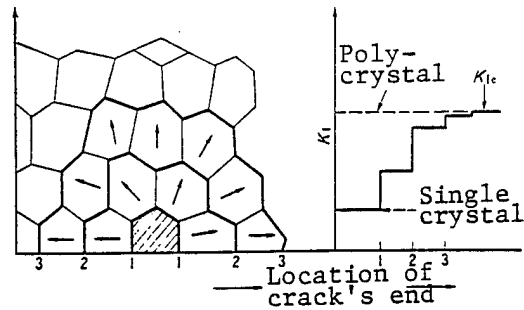


Figure 2. Change of  $K_{Ic}$  Due to Crack's Length

The mechanism to be considered next for toughening ceramics is the method of improving  $K_{Ic}$  by dispersing the second phase or heterogeneous particles (crystal particles of different shapes and size, though they are of the same substance), i.e., a compounding method. This mechanism can be divided broadly into two: one uses metal as the dispersing material and the other ceramics. The former is a toughening method that has concentrated stress at the end of a crack absorbed by utilizing the plastic deformation of a metal. The most important factor of this mechanism is that a crack should spread inside the metallic phase. The material that made the best use of this method is sintered hard metal (cermet), in which a thin Co film of 5 to 15 wt percent surrounds a particle of WC, and has achieved a  $K_{Ic}$  value of about  $20 \text{ MN/m}^{3/2}$ . The research for toughening ceramics with this method has been carried out by many people to date, but a substantial amount of metal should be dispersed in order to toughen ceramics with this method. The toughening of ceramics by this mechanism, however, results in sacrificing some excellent properties of ceramics, so it does not agree with the basic way of thinking about the toughening of ceramics mentioned in the preceding chapter. On the other hand, the latter is a toughening method that disperses ceramics in ceramics. Accordingly, the essential properties of ceramics will not be lost by applying this mechanism.

The mechanism for toughening ceramics by compounding ceramics with ceramics can be classified into two: 1) One is to develop "pinning," "bending," and "deflection" at the end of a crack through the interaction between the end of a crack and a dispersed phase, and 2) the other is to relax concentrated stress at the end of a crack (or to control the development of a crack with generated compressive stress) by developing the "crystal modification of a dispersed phase (tetragonal crystal  $\text{ZrO}_2$ )," "a microcrack," and the "pullout of a whisker or fiber" in the process zone near the end of a crack. In the case of 1), the question of what mechanism out of the three introduced above is effective will be decided by the residual stress around the dispersed phase, which occurs when the material cools down from the manufacturing temperature, due to the anisotropy or differences of the thermal expansion coefficient and Young's modulus between the matrix and dispersed phase. Figure 3 shows the typical interaction between the end of a crack and a dispersed phase. Figure 4 shows the pinning effect at the end of a crack, which is observed in composite ceramic glass of a cordierite system. These cracks show no growth since they were pinned down by crystal particles, even though

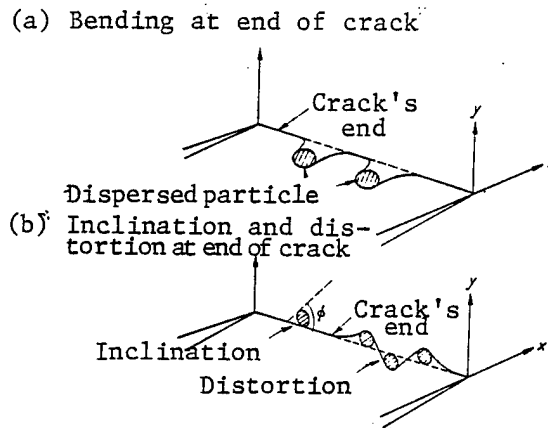


Figure 3. Interaction Between Crack's End and Dispersed Particle

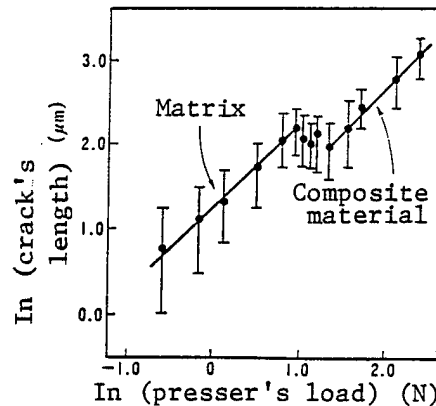


Figure 4. Changes in Lengths of Cordierite Glass/Ceramics Composite Material Due to Load of Vickers Presser

the load of the Vickers presser increased within the range of about 3 to 4 N, thus increasing  $K_{IC}$  by about 1.5 times. Moreover, the improvement of  $K_{IC}$  due to the deflection of the end of the crack largely depends on the shape of the dispersed phase. With respect to the shape of the dispersed phase, a cylindrical shape is more effective than a discoid shape and a discoid shape is more effective than a granule shape.

The details of the toughening mechanism to improve  $K_{IC}$  by preventing external stress through the formation of a process zone near the end of a crack are expected to be explained in the special edition of this magazine by Sato, Shimada, and Miyata, so this article will only indicate each mechanism, as shown in Figure 5. The conception of toughening ceramics by means of whiskers or fibers is entirely different from the case where the matrix is metallic or plastic. The metallic or plastic matrix is aimed at load transfer effects by utilizing the highly elastic coefficient and high strength of whiskers and fibers. So, it is not desirous that the pullout of whiskers or fibers occurs,

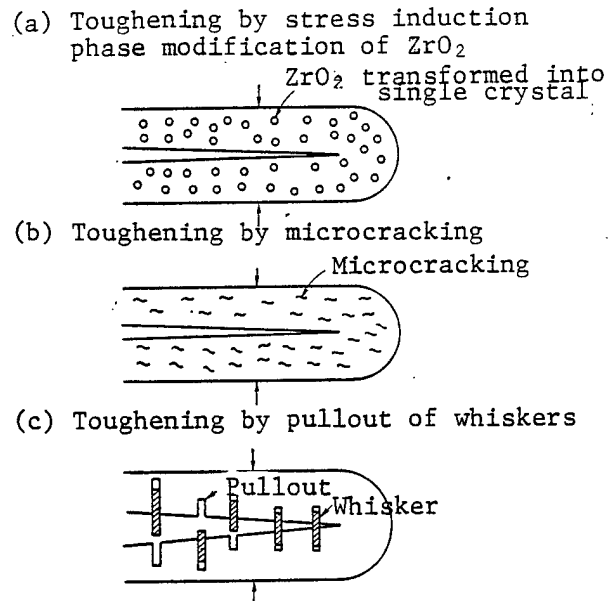


Figure 5. Toughening by Preventing External Stress Through Formation of Process Zone

as shown in Figure 5(c). On the otherhand, in the case of a ceramic matrix, the pullout of whiskers or fibers in the vicinity of the end of a crack is most important, as shown in Figure 5(c). Naturally, however, the deflection of a crack plays an important role in this case.

### 2.3 From Homogeneous to Heterogeneous Organization

When reviewing these various ceramic toughening mechanisms introduced in the preceding chapter, it was found that the  $K_{IC}$  of ceramics can be generally improved by making the organization heterogeneous and generating the partial fracture of  $K_{II}$  and  $K_{III}$  modes, as shown in Figure 6(a). However, when the organization is made heterogeneous, the size of the crack which becomes a fracture source increases like the curve given in Figure 6(b). Therefore, it is generally very difficult to manufacture tough ceramics by associating the toughening with the strengthening of ceramics. In order to develop tough ceramics it is necessary to develop a curve similar to curve (2) in Figure 6(b) by controlling the cracks as much as possible which develop in the process of toughening or their growth. If such a curve is produced, tough ceramics can be developed by associating toughening with strengthening like curve (2) of Figure 6(b). This indicates that it is important not to increase the size of the critical crack of the matrix by making the organization heterogeneous. Figure 7 gives an example of fracture strength being improved by 30 percent under such an idea by dispersing discoid shaped  $Al_2O_3$  in  $Al_2O_3$  and by improving  $K_{IC}$  by making the organization heterogeneous. Furthermore, when dispersing 41  $\mu m$  discoid shaped  $Al_2O_3$ , fracture strength decreases by dispersing discoid shaped  $Al_2O_3$  even slightly, since the contribution of the expanded size of the critical crack is large.



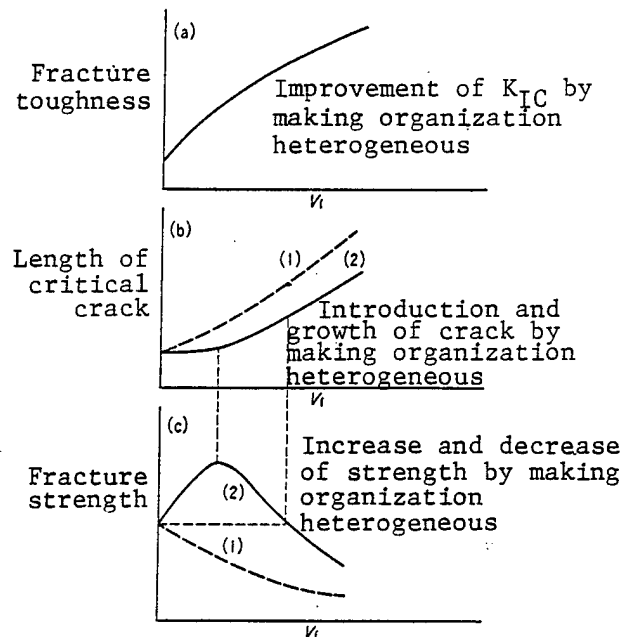


Figure 6. Fracture Toughness Due to Increased Dispersed Phases (a), Length of Critical Crack (b), and Changes in Fracture Strength (c)

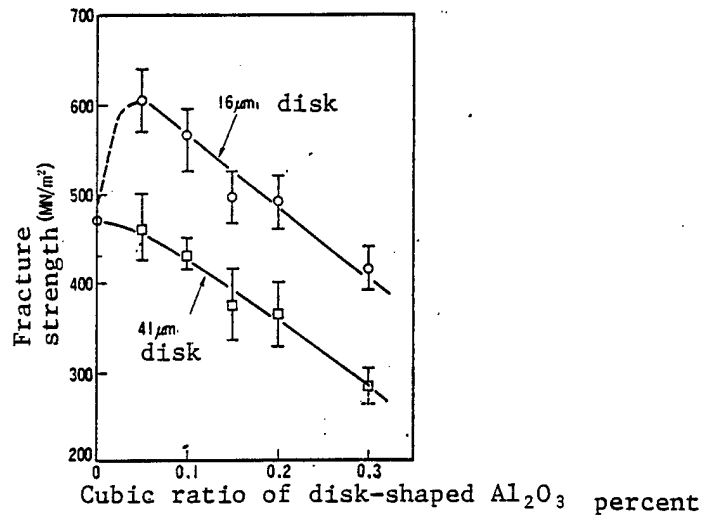


Figure 7. Fracture Strength of  $Al_2O_3$  Dispersing Discoid Shape  $Al_2O_3$

The above review indicates that the microstructure of ceramics should be heterogeneous as long as the size of the critical crack is not increased.

## 2.4 Present Status of Toughening Ceramics

As a result of energetic research by Western ceramists, many kinds of tough ceramics have recently been developed by using various toughening mechanisms. Some of the results of these efforts, which were reported recently, are introduced in Table 2.

Table 2. Tough Ceramics Recently Developed

Ceramics	$K_{IC}$ (MN/m <sup>3/2</sup> )	Toughening mechanism	Footnote
Si <sub>3</sub> N <sub>4</sub>	4→6	Deflection of crack due to cylindrical particle	9
SiC	4→6	Same as above	10
PSZ (Y <sub>2</sub> O <sub>3</sub> )	1→10	Stress induction modification of ZrO <sub>2</sub>	11
Al <sub>2</sub> O <sub>3</sub> /PSZ	3.5→8.0	Same as above	12
Al <sub>2</sub> O <sub>3</sub> /SiC whisker	3.5→8.7	Deflection of crack, pullout of whisker	13
Mullite/SiC whisker	2.8→4.4	Same as above	11
TZP*/SiC whisker	6.8→11.0	Same as above	11
LAS**/SiC fiber	1.2→24	Pullout of fiber	14

\* Tetragonal Zirconia Polycrystal

\*\*Lithium Aluminum Silicate crystal glass

With respect to SiC and Si<sub>3</sub>N<sub>4</sub> ceramics, which are drawing attention as high temperature structural materials, a material with a  $K_{IC}$  of more than 6 MN/m<sup>3/2</sup> has been developed through the toughening method to cause the deflection of ceramics by growing particles of a cylindrical shape (making the organization heterogeneous) without increasing the size of the critical cracks.

In the case of partially stabilized ZrO<sub>2</sub> (PSZ), a  $K_{IC}$  value of more than 10 MN/m<sup>3/2</sup> is reported, but this mechanism is only effective under transformation temperatures from a monolinal crystal to a tetragonal crystal, and vice versa. This material, therefore, is classified as a low temperature material. TZP (Tetragonal Zirconia Polycrystal)/SiC whiskers are being studied for the purpose of making up for this ZrO<sub>2</sub> defect. From this group the  $K_{IC}$  value of 11.0 MN/m<sup>3/2</sup> has been obtained, but the strength declined by about half. This is considered attributable to the reaction in the air between ZrO<sub>2</sub> and SiC at a high temperature. Therefore, efforts to improve the  $K_{IC}$  and strength of ZrO<sub>2</sub> ceramics under high temperatures are not yet successful.

One of the most remarkable progresses in this field in recent years is the toughening of oxide ceramics by means of SiC whiskers or fibers. In the case of whisker-reinforced Al<sub>2</sub>O<sub>3</sub>, as is clear from Table 2, a value of 8 MN/m<sup>3/2</sup> -9 has been obtained, which is nearly close to the  $K_{IC}$  value obtained through the stress inductive phase modification mechanism of ZrO<sub>2</sub>. While in the case of aluminum silicate crystal glass, a  $K_{IC}$  value as high as 24 MN/m<sup>3/2</sup>, which is higher than that of sintered hard metal, has been obtained by compounding

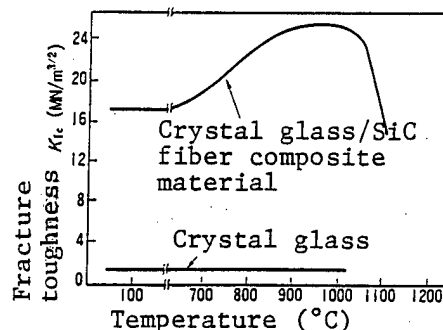


Figure 8. Change of Fracture Toughness According to Temperature of Lithium Aluminum Silicate Crystal Glass/SiC Fiber Composite Material

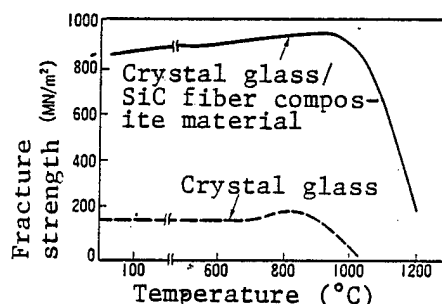


Figure 9. Change of Fracture Strength According to Temperature of Lithium Aluminum Silicate Crystal Glass/SiC Fiber Composite Material

SiC fibers. Additionally, toughening by using these material groups has achieved remarkably high strength. Figures 8 and 9 show changes according to temperature in  $K_{IC}$  and fracture strength, respectively, of lithium aluminum silicate crystal glass compounded with SiC fibers (trade name: Nikaron) developed in Japan. Even at a high temperature of 1,000°C,  $K_{IC}$  shows more than 16 MN/m<sup>3/2</sup> and fracture strength shows 700 MN/m<sup>3/2</sup>, both of which are very high values.

However, these values were obtained in inactive gas and it is reported that when measuring in the air, they drop considerably at temperatures of more than 600°C because of altered SiC fibers due to oxidation. Figure 10 shows changes in fracture strength, according to temperature, of the composite material of crystal glass consisting of BaMg<sub>2</sub>Al<sub>6</sub>Si<sub>9</sub>O<sub>13</sub> and SiC fibers. This crystal glass is the material which has been newly developed in consideration of the properties matching Nikaron, and in this case its fracture strength lowered at temperatures over 600°C in the air, as is shown in Figure 10.

As is clear from Table 1, the toughening and strengthening of ceramics by use of long fibers is considered most effective and has the best results out of all the other mechanisms. However, in order to make the most of this mechanism in not only glass but oxide and nonoxide ceramics, it is necessary to develop high strength fibers able to stand higher temperatures and a new production process designed to evenly distribute fibers.

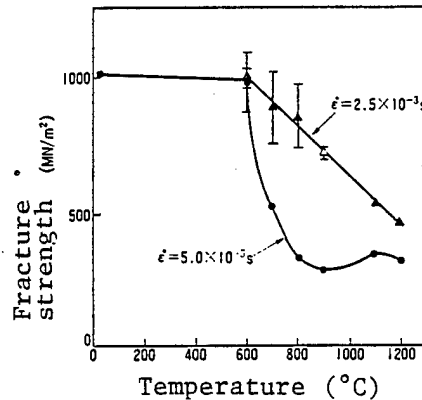


Figure 10. Change of Fracture Strength in Air According to Temperature of Composite Material of Crystal Glass Comprising  $\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{13}$  With SiC Fiber (30 vol percent)

The control of microstructures, the stress-strain curves of materials dispersing the second phase of either a granule or laminar shape with a comparably small aspect ratio are assumed to become like (a) and (b) of Figure 11, even though  $K_{IC}$  has substantially been improved. However, the stress-strain curve of the compounded material with either whiskers having a long aspect ratio or fibers is assumed to develop a form that looks like, at a glance, a ductility fracture of metal, as shown in Figure 11(c). In other words, a microfracture is considered to result in a permanent macroscopic deformation. If such a fracture develops, then this fracture is considered to be easily controllable, even slightly.

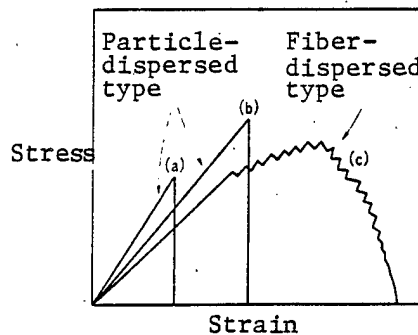


Figure 11. Stress-Strain Curves of Composite Materials Toughened by Dispersing Particles and Fibers

### 3. Necessity of Multiple Toughening

The  $K_{IC}$  value which can be achieved by the toughening method other than the pullout of fibers, for which new long fibers and a manufacturing process need to be developed, is about 6 to 10  $\text{MN/m}^{3/2}$ . Therefore, in order to develop structural ceramics with a high  $K_{IC}$  value of 20 to 30  $\text{MN/m}^{3/2}$ , multiple toughening is necessary where multiple, not single, toughening mechanisms work independently without interfering with others.

There are cases where this multiple toughening is already occurring unintentionally in actual material. An example is toughening by the two mechanisms of the deflection of a crack and the phase modifications of  $ZrO_2$ , which occur when dispersing  $ZrO_2$ . The multiple toughening will be examined as follows concerning the  $Al_2O_3/ZrO_2/SiC$  whisker composite material presently being handled by the author.

The effects which can be expected when dispersing  $ZrO_2$  in  $Al_2O_3$  are as follows:

- (1) The growth of particles of  $Al_2O_3$  can be controlled by using matrix  $ZrO_2$  which is distributed over the peculiar points of a microstructure, such as grain boundary triple points.
- (2) Toughening by crack deflection caused by  $ZrO_2$ .
- (3) Toughening by phase modification of  $ZrO_2$ .
- (4) Acceleration of sintering by means of  $ZrO_2$ .

On the other hand, the part  $SiC$  whiskers play is assumed as follows:

- (5) Toughening by crack deflection caused by  $SiC$  whiskers.
- (6) Toughening by the pullout of  $SiC$  whiskers in a high temperature range where the toughening by the phase modification of  $ZrO_2$  is not applicable.
- (7) The control of SCG by  $SiC$  whiskers.

Additionally, in order that these mechanisms work and roles are played without interfering with others, the method for compounding raw materials should be considered as follows:

- (8) To distribute  $ZrO_2$  and  $SiC$  whiskers evenly in  $Al_2O_3$ .
- (9) To evenly cut the whiskers in proper lengths in order that the roles referred to in Items (5) and (6) be played in full.

The authors have succeeded in developing an  $Al_2O_3/ZrO_2/SiC$  whisker composite material with a high  $K_{IC}$  value and tolerance of high temperatures by utilizing nearly in full the roles  $ZrO_2$  and  $SiC$  whiskers play as mentioned above.

Concepts for multiple toughening are expected to become very important in the future. Of course, there are cases where such a combination is not desirous or a combination does not work synergistically. However, if the study on the combination of toughening mechanisms which can match matrixes and independently exist continues to be carried out, it may be possible to raise the  $K_{IC}$  values of ceramics to more than  $20 \text{ MN/m}^{3/2}$ . For this purpose it is necessary, of course, to develop a new manufacturing process.

#### 4. From Micron to Nanometer

Research for toughening ceramics has so far paid attention only to the control of the structure of a micron order, aside from the grain boundary. However, if the control of a small structure or of a nanometer level inside a crystal particle is considered, the possibility of further improving the toughness of ceramics increases. Such examples include: laminating the second phase according to a nanometer order in a crystal particle, compounding the second phase of a nanometer order into a cylindrical or whisker shape in a crystal particle, or introducing twins or stacking faults into a crystal particle. This is an effort to improve the brittleness of ceramics in a little more substantial way by controlling the structure of a crystal particle considered to be the minimum unit of ceramics. The improvement of the  $K_{IC}$  of ceramics by this method will be discussed in detail by Niihara and Hirai in the special edition of this magazine.

By using a special method known as CVD for obtaining a solid from gas, Tohoku University Metallic Material Research Laboratory, which the author belonged to until March 1986, has succeeded in synthesizing composite ceramics with various kinds of nanometer levels, as shown in Figure 12. Therefore, if the research in this field, or on powder synthesis in particular, makes progress in the future, the author is confident that it will become possible to markedly improve the brittleness of a crystal particle itself.

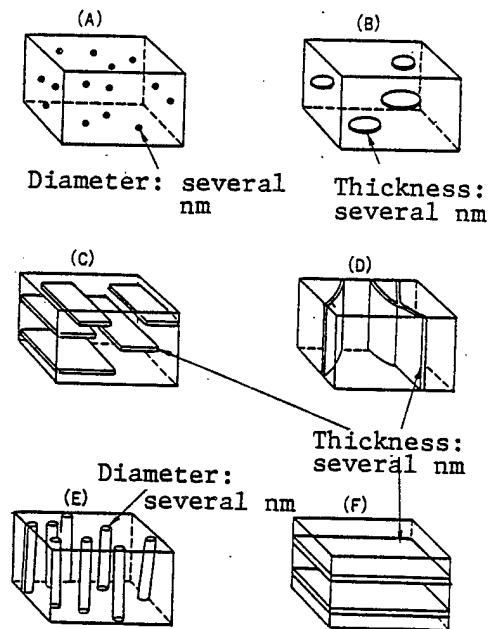


Figure 12. Various Composite Materials in Nanometer Particles, Synthesized by CVD Method

## 5. Conclusion

Part of the author's idea about brittleness improvement and the toughening and strengthening of ceramics has been introduced. Except for matters which have already been accepted as correct through research done until now, the author wrote about matters yet unclarified, based on his own intuition or wishes. The author believes there are many readers who do not agree with him on many points and would be happy to receive any direct inquiries.

The research on toughening ceramics has made rapid strides in the past 10 years. This research changed from the improvement of toughness by controlling microstructures to that of utilizing the modification of  $ZrO_2$ , and in recent years the improvement of toughness by means of whiskers and fibers has begun to interest many people. Research on multiple toughening is also being carried out. With respect to the relation between microstructures and fracture toughness, the control of microstructures that are smaller than the ones that have been handled up until now by a magnitude of three digits is being taken up for study. These research activities are expected to bear fruit in the near future and lead to the advent of ceramics which are of high mechanical reliability and very high toughness.

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CSO: 4306/3642

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